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Thermodynamics of formation of solid solutions between $BaZrO_3$ and $BaPrO_3$

A linear relationship between the standard enthalpy of formation from binary oxides, $\Delta_f H°_{ox}$, and the Goldschmidt tolerance factor, t, for some $A^{II}B^{IV}O_3$ (A = Ca, Sr, Ba; B = Ti, Zr, Hf, Ce, Pr, Tb, U, Pu, Am) perovskite oxides was used for estimation of $\Delta_f H°_{ox}$ of Pr-substituted barium zirconates $BaZr_{1-x}Pr_xO_3$. A dependence of the relative change of the standard entropies, $S°_{298}$, on the relative change of the molar volumes in the reactions of formation of $A^{II}B^{IV}O_3$ (A = Ca, Sr, Ba; B = Ti, Zr, Hf, Ce) from binary oxides was also found to be linear. Using this dependence, a relatively precise method of estimating $S°_{298}$ was proposed, and $S°_{298}$ of $BaPrO_3$ was calculated as (162.8 ± 2.8) $J \cdot mol^{-1} \cdot K^{-1}$. Knowing $S°_{298}$ of $BaPrO_3$ and using the literature data for $S°_{298}$ of $BaZrO_3$, the values of $S°_{298}$ of $BaZr_{1-x}Pr_xO_3$ were predicted on the assumption that $BaZr_{1-x}Pr_xO_3$ is a regular or ideal solution of $BaPrO_3$ in $BaZrO_3$ as evidenced by the very small enthalpy of mixing calculated based on the estimated $\Delta_f H°_{ox}$. The values of standard entropy changes, $\Delta_f S°_{ox}$, and Gibbs energy changes, $\Delta_f G°_{ox}$, for the reactions of formation of $BaZr_{1-x}Pr_xO_3$ from BaO, ZrO_2 and PrO_2 were also estimated. Substituting Pr for Zr in $BaZr_{1-x}Pr_xO_3$ results in $\Delta_f H°_{ox}$ and $\Delta_f G°_{ox}$ becoming more positive, indicating the decrease of the relative stability with respect to the corresponding binary oxides. Expanded uncertainties of the estimated values of $\Delta_f H°_{ox}$ and $\Delta_f G°_{ox}$ are equal to 14 $kJ \cdot mol^{-1}$, and those of $S°_{298}$ and $\Delta_f S°_{ox}$ — less than 2.8 $J \cdot mol^{-1} \cdot K^{-1}$ and 3.5 $J \cdot mol^{-1} \cdot K^{-1}$, respectively, for $BaZr_{1-x}Pr_xO_3$ (x = 0.0–1.0).

Keywords: doped barium zirconate; thermodynamics; thermodynamic properties prediction

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Introduction

Partially substituted barium zirconates, $BaZr_{1-x}M_xO_{3-\delta}$ (M = rare-earth or alkaline-earth element), are the state-of-the-art proton-conducting electrolyte materials for intermediate-temperature solid oxide fuel cells [1–3]. These complex oxides possess high proton conductivity upon hydration, good chemical and mechanical stability. Among their known drawbacks are high grain boundary resistance, slow

grain growth and, as a consequence, very high sintering temperatures (1900–2000 K) required for obtaining dense ceramics [4–8]. Praseodymium doping was suggested as a possible way not only to overcome these drawbacks [9] but also, due to potentially mixed-valent state of Pr, to obtain triple-conducting (electron-proton-oxide ion) and catalytically active electrode materials for highly efficient proton-conducting solid oxide fuel cells (PC SOFCs) [10, 11]. In spite of the promising electrochemical properties of the $BaZr_{1-x}Pr_xO_3$ zirconates [10, 11], the influence of Pr doping on their thermodynamics of formation is still unknown. At the same time, understanding the thermodynamics of key materials for PC SOFCs is of utmost importance for the assessment of the long-term behavior of the whole device. Some thermodynamic properties of $BaZr_{1-x}Pr_xO_3$ oxides such as enthalpy increments and constant-pressure heat capacities have been studied by us earlier [12]. This work continues systematic investigation of the influence of Pr doping on the thermodynamics of barium zirconates and was aimed to estimate the standard thermodynamic functions (enthalpy, entropy and Gibbs free energy) of formation of $BaZr_{1-x}Pr_xO_3$ oxides.

Results and discussion

Typically, when it is necessary to experimentally determine the standard formation enthalpy of a compound, the solution calorimetry is the most straightforward method of choice. However, the dissolution of zirconates is quite a hard task, as our preliminary experiments showed. It requires using either highly corrosive mixtures of acids such as, for example, HF and HNO_3 employed by Huntelaar et al. [13], or high-temperature melts [14]. Importantly, in the latter case the solvent stirring is necessary since the dissolution kinetics is slow. Unfortunately, neither of the above mentioned possibilities was available for the authors. Indeed, the measurements on MHTC 96 (Setaram, France) calorimeter, in which the solvent stirring is not implemented, resulted in irreproducible solution enthalpies of $BaZr_{1-x}Pr_xO_3$. Besides, the hydrofluoric acid resistant measurement cell for the solution calorimeter has to be custom-made and was not readily available. Because of these reasons, the standard formation enthalpies of $BaZr_{1-x}Pr_xO_3$ zirconates were estimated using the well-known strong correlation between the formation enthalpy and Goldschmidt's tolerance factor [15–18]. This correlation was shown to allow predicting reasonably good, i.e. very close to the experimental values, estimates of the formation enthalpies for many perovskite oxides.

The standard enthalpy of formation at 298.15 K, $\Delta_f H^\circ_{ox}$, corresponding to the reaction

$$AO + BO_2 = ABO_3 \qquad (1)$$

calculated for a number of $A^{II}B^{IV}O_3$ perovskite-type oxides, is shown in Fig. 1 as a function of Goldschmidt's tolerance factor, $t = \frac{r_A + r_0}{\sqrt{2}\left(r_B + r_0\right)}$. The values of the tolerance factor were calculated using the crystal radii reported by Shannon [19] with the following coordination numbers: 12 — A^{2+} cation, 6 — for both B^{4+} cation and O^{2-} anion. The necessary thermodynamic data were taken from [20–27]. It should be noted that while the AO oxides (namely, CaO, SrO and BaO) belong to the same rock-salt crystal structure class, it is not the case for BO_2 and ABO_3 oxides which possess different crystal structure depending on the nature of the A and B cations.

However, the differences in the crystal structure of both BO_2 and ABO_3 with different cations were not taken into account. The enthalpies of slight distortions of the perovskite structure in ABO_3 are generally small and were thought to be much less than the standard deviation of the estimated values. In turn, even though the crystal structure of BO_2 varies more than that of ABO_3, judging by the good linearity of the $\Delta_f H^\circ_{ox},(t)$ dependence in Fig. 1, its influence should also be rather small.

The linear dependence observed in Fig. 1 was least squares fitted. The resulting equation is the following:

$$\Delta_f H^\circ_{ox} \Big/ \left(\mathrm{kJ \cdot mol^{-1}}\right) = 793.8 - 907.2 \cdot t \quad (2)$$

with the coefficient of determination $R^2 = 0.98$. The standard formation enthalpies of $BaZr_{1-x}Pr_xO_3$ oxides calculated according to Eq. (2) are summarized in Table 1. The standard deviation of the fitted line from the points in Fig. 1 was found to be 7 kJ·mol^{-1}; therefore, the expanded uncertainty (95% confidence level) of the $\Delta_f H^\circ_{ox}$ values reported in Table 1 is equal to 14 kJ·mol^{-1}. However, since the experimental points corresponding to both $BaZrO_3$ and $BaPrO_3$ in Fig. 1 deviate from the fitted line (i.e. from Eq. (2)) by less than 5.6 kJ·mol^{-1}, the accuracy of our predicted $\Delta_f H^\circ_{ox}$ values is likely to be somewhat better than this rather conservative estimate of 14 kJ·mol^{-1}.

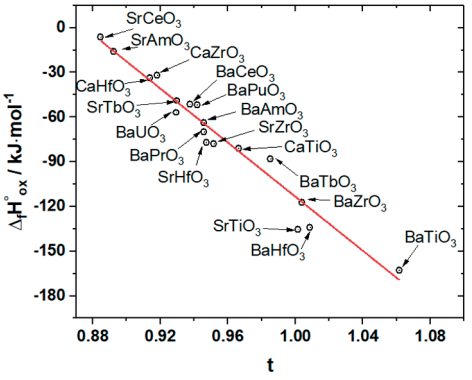

Fig. 1. Standard enthalpy of formation from binary oxides vs tolerance factor for some $A^{II}B^{IV}O_3$ oxides. Points — calculation using the literature data [20–27], line — linear fit. The reference thermodynamic data values are also given in Supplementary

As follows from Fig. 1 and Table 1, the standard formation enthalpy of zirconates $BaZr_{1-x}Pr_xO_3$ increases with doping level, x, becoming less negative. This corresponds to increasing distortions of the perovskite lattice, as evidenced by the results of the structural studies [28, 29] and the gradual decrease of the tolerance factor, t, from the value of 1, characteristic of undoped $BaZrO_3$ possessing ideal cubic perovskite structure, to 0.946 for $BaPrO_3$ with orthorhombic distortions of the lattice. Similar, but significantly more pronounced trend — the decrease in $\Delta_f H^\circ_{ox}$ with the increase in x — was also reported for $BaZr_{1-x}Y_xO_{3-\delta}$ (x = 0.0–0.3) [14]. In contrast with $BaZr_{1-x}Pr_xO_3$, the structure of $BaZr_{1-x}Y_xO_{3-\delta}$ is destabilized not only by the difference in crystal radii of Zr and Y, but also by the formation of the oxygen vacancies. Moreover, Ba-loss during synthesis procedure and associated Y redistribution between A- and B-sublattice, not to mention of ordering of oxygen vacancies, are also influencing the stability of $BaZr_{1-x}Y_xO_{3-\delta}$. These additional factors should be responsible for more abruptly increasing $\Delta_f H^\circ_{ox}$ of $BaZr_{1-x}Y_xO_{3-\delta}$ with the dopant concentration, as compared to $BaZr_{1-x}Pr_xO_3$.

It is also of interest that the mixing enthalpy of $BaZr_{1-x}Pr_xO_3$ solid solution, calculated as

$$\begin{aligned}\Delta_{mix} H^\circ = \Delta_f H^\circ_{ox}\left(BaZr_{1-x}Pr_xO_3\right) - \\ -(1-x)\cdot\Delta_f H^\circ_{ox}\left(BaZrO_3\right) - \\ -x\cdot\Delta_f H^\circ_{ox}\left(BaPrO_3\right),\end{aligned} \quad (3)$$

is slightly positive, as seen in Table 1, most probably, as a result of both the abovementioned difference in the crystal structure of the end members and the size mismatch between Zr^{4+} and Pr^{4+}cations. However, the absolute value of $\Delta_{mix}H°$ is well within the estimated level of uncertainty, indicating the behavior close to that of the ideal or regular (the maximum of $\Delta_{mix}H°$ corresponds to $x = 0.5$) solution. This is consistent with a very small positive change of the molar volume upon mixing $BaZrO_3$ and $BaPrO_3$ [28]. The ideal (or regular) solution behavior opens up a possibility to estimate the entropy of $BaZr_{1-x}Pr_xO_3$ solid solution as

$$S^{\circ}_{(BaZr_{1-x}Pr_xO_3)} = \\ = -R\left[x\cdot\ln(x)+(1-x)\cdot\ln(1-x)\right]+ \\ +(1-x)\cdot S^{\circ}_{(BaZrO_3)}+x\cdot S^{\circ}_{(BaPrO_3)}, \quad (4)$$

where R is the universal gas constant, the first term in the right hand side is the entropy of ideal mixing and $S^{\circ}_{(BaZrO_3)}$ and $S^{\circ}_{(BaPrO_3)}$ — the standard entropies of $BaPrO_3$ and $BaPrO_3$, respectively.

Table 1

Estimated standard thermodynamic functions of $BaZr_{1-x}Pr_xO_3$ ($x = 0.0–1.0$)

x	t[a]	$\Delta_fH°_{ox}$[b] / kJ·mol^{-1}	$\Delta_fH°_{el}$[c] / kJ·mol^{-1}	$\Delta_{mix}H°$[d] / kJ·mol^{-1}	$S°_{298}$[e] / J·mol^{-1}·K^{-1}	$\Delta_fS°_{ox}$[f] / J·mol^{-1}·K^{-1}	$\Delta_fG°_{ox}$[g] / kJ·mol^{-1}
0.0	1.004	— 117.0*	–1762.5	0.00	125.5	5.1	–118.5
0.1	0.998	–111.4	–1742.1	0.29	131.9	8.5	–113.9
0.2	0.992	–106.0	–1721.8	0.51	137.1	10.7	–109.2
0.3	0.986	–100.5	–1701.6	0.67	141.8	12.3	–104.2
0.4	0.980	–95.2	–1681.4	0.76	146.0	13.5	–99.2
0.5	0.974	–89.9	–1661.3	0.78	149.9	14.3	–94.2
0.6	0.968	–84.7	–1641.3	0.75	153.5	14.8	–89.1
0.7	0.963	–79.5	–1621.3	0.65	156.7	15.0	–84.0
0.8	0.957	–74.4	–1601.4	0.49	159.5	14.8	–78.8
0.9	0.951	–69.4	–1581.5	0.28	161.8	14.0	–73.6
1.0	0.946	— 64.4**	–1561.7	0.00	162.8	12.0	–68.0

[a] Goldschmidt's tolerance factor, (crystal radii, coordination numbers: 12 — for A^{2+} cation, 6 — for B^{4+} cation and O^{2-} anion). [b] Standard enthalpy of formation from binary oxides at 298.15 K, the expanded uncertainty (95% confidence level) is ±14 kJ·mol^{-1}. [c] Standard enthalpy of formation from elements at 298.15 K, the expanded uncertainty (95% confidence level) is ±14 kJ·mol^{-1}. [d] Standard enthalpy of mixing at 298.15 K, the expanded uncertainty (95% confidence level) is ±14 kJ·mol^{-1}. [e] Standard entropy at 298.15 K, the expanded uncertainty (95% confidence level) linearly scales with x from ±1 J·mol^{-1}·K^{-1} for $BaZrO_3$ ($x = 0$) to ±2.8 J·mol^{-1}·K^{-1} for $BaPrO_3$ ($x = 1$). [f] Standard entropy of formation from binary oxides at 298.15 K, the expanded uncertainty (95% confidence level) linearly scales with x from ±1.2 J·mol^{-1}·K^{-1} for $BaZrO_3$ (x=0) to ±3.5 J·mol^{-1}·K^{-1} for $BaPrO_3$ ($x = 1$). [g] Standard Gibbs free energy of formation from binary oxides at 298.15 K, the expanded uncertainty (95% confidence level) is ±14 kJ·mol^{-1}.

* Experimental formation enthalpy $\Delta_fH°_{ox}$ = (— 115.12 ± 3.69) kJ·mol^{-1} [14], (–117.44 ± 3.7) kJ·mol^{-1} [13]

** Experimental formation enthalpy $\Delta_fH°_{ox}$ = (— 70 ± 10) kJ·mol^{-1} [20], (–147 ± 8) kJ·mol^{-1} [21]

The only unknown parameter in the Eq. (4) is the standard entropy of $BaPrO_3$, $S^\circ_{(BaPrO_3)}$, which has to be estimated since no experimental value has been reported so far. To do this, we, first, tried to correlate the standard entropies available for some of the $A^{II}B^{IV}O_3$ oxides with their molar volumes in line with the so-called volume-based approach introduced by Glasser and Jenkins [30]. However, it was found that much better correlation can be established using relative changes of entropy and molar volume instead of their absolute values. These relative changes correspond to the formation from binary oxides (reaction (1)) and can be calculated as follows:

$$\omega_S = \frac{\Delta_f S^\circ_{ox}}{S^\circ_{AO} + S^\circ_{BO_2}}, \qquad (5)$$

$$\omega_V = \frac{\Delta_f V_{m(ox)}}{V_{m(AO)} + V_{m(BO_2)}}, \qquad (6)$$

where ω_S and ω_V are the relative changes of entropy and molar volume; $\Delta_f S^\circ_{ox}$ and $\Delta_f V_{m(ox)}$ are the absolute changes of standard entropy and molar volume in the formation reaction (1); S°_{AO}, $S^\circ_{BO_2}$ and $V_{m(AO)}$, $V_{m(BO_2)}$ — are standard entropies and molar volumes of constituting binary oxides, respectively. ω_S as a function of ω_V is shown in Fig. 2 for the $A^{II}B^{IV}O_3$ oxides for which we have managed to find the literature values of the absolute entropies. Surprisingly good linear correlation can be observed between ω_S and ω_V. The two outliers are $CaHfO_3$ and $BaTiO_3$. The reason for these deviations is unclear, but, taking into account the good linear trend for the rest of the $A^{II}B^{IV}O_3$ oxides, it seems that one can suggest some errors in the reference data reported for $BaTiO_3$ and $CaHfO_3$.

The observed $\omega_S(\omega_V)$ linear dependence (see Fig. 2) was least squares fitted. The resulting equation is the following:

$$\omega_S = 7.99 \cdot 10^{-2} + 0.51 \cdot \omega_V. \qquad (7)$$

The coefficient of determination is $R^2 = 0.97$. The standard deviation of the fitted line from the points in Fig. 2 is 0.006 (note that $BaTiO_3$ and $CaHfO_3$ were not taken into account). The absolute entropy of the perovskite oxide $A^{II}B^{IV}O_3$ can be calculated using the Eq. (7) as

$$S^\circ_{ABO_3} = \left(S^\circ_{AO} + S^\circ_{BO_2}\right) + \Delta_f S^\circ_{ox} = \\ = \left(S^\circ_{AO} + S^\circ_{BO_2}\right)\left(1.0799 + 0.51 \cdot \omega_V\right). \qquad (8)$$

The standard deviation of the as-estimated entropy from the experimental reference data does not exceed 0.5 $J \cdot mol^{-1} \cdot K^{-1}$. For the outliers, $BaTiO_3$ and $CaHfO_3$, calculation according to Eq. (8) leads to the standard entropies 120.6 $J \cdot mol^{-1} \cdot K^{-1}$ and 107.0 $J \cdot mol^{-1} \cdot K^{-1}$, respectively, with the deviations from the reference thermodynamic data [20–27,31–34] equal to +12.7 $J \cdot mol^{-1} \cdot K^{-1}$ (i.e. +11.8%) and –6.4 $J \cdot mol^{-1} \cdot K^{-1}$ (i.e. –5.7%), respectively.

The absolute entropy of $BaPrO_3$, calculated using Eq. (8), equals 162.8 $J \cdot mol^{-1} \cdot K^{-1}$

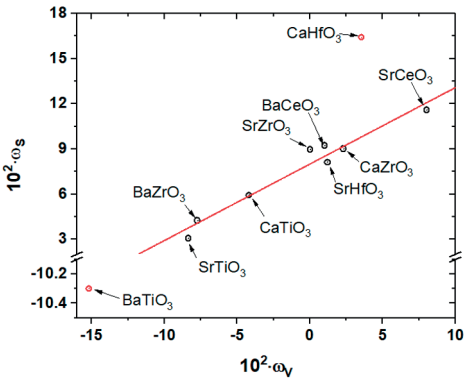

Fig. 2. Relative change of entropy vs relative change of molar volume in the reaction (1) for some $A^{II}B^{IV}O_3$ perovskites. Points — calculation using the literature data [20–27, 31, 32], line — linear fit. The reference thermodynamic and structural data values are also given in Supplementary

with probable expanded uncertainty (95% confidence level) of 2.8 J·mol^{-1}·K^{-1}. Here, rather high uncertainty of the $S^\circ_{PrO_3}$ value (2.0 J·mol^{-1}·K^{-1} [34]) has the most influence on the expanded uncertainty of $S^\circ_{BaPrO_3}$. With this value in hand, it is now possible to estimate the entropies of $BaZr_{1-x}Pr_xO_3$ solid solutions, S°_{298}, according to Eq. (4). The calculated values are summarized in Table 1. The combined uncertainty of S°_{298} depends on the amount of dopant x in $BaZr_{1-x}Pr_xO_3$, and can be evaluated using the following expression:

$$\delta(S^\circ_{298}) = \sqrt{\left((1-x)\cdot\delta(S^\circ_{BaZrO_3})\right)^2 + \left(x\cdot\delta(S^\circ_{BaPrO_3})\right)^2}, \quad (9)$$

where $\delta(S)$ is the uncertainty of the corresponding entropy value S. With the values of $\delta(S^\circ_{BaZrO_3})$ = 1.0 J·mol^{-1}·K^{-1} [32], which is less than our predicted value of $\delta(S^\circ_{BaPrO_3})$ = 2.8 J·mol^{-1}·K^{-1}, $\delta(S^\circ_{298})$ is also less than 2.8 J·mol^{-1}·K^{-1} for any possible value of x.

The entropies of formation from oxides, $\Delta_f S^\circ_{ox}$, listed in Table 1, obviously, also depend on the concentration of praseodymium:

$$\Delta_f S^\circ_{ox} = S^\circ_{298}\left(BaZr_{1-x}Pr_xO_3\right) - S^\circ_{298}(BaO) - (1-x)\cdot S^\circ_{298}(ZrO_2) - x\cdot S^\circ_{298}(PrO_2), \quad (10)$$

and so does their uncertainty, which increases with x from 1.2 J·mol^{-1}·K^{-1} for $BaZrO_3$ to 3.5 J·mol^{-1}·K^{-1} for $BaPrO_3$.

The standard Gibbs free energy of formation at 298.15 K of $BaZr_{1-x}Pr_xO_3$ oxides, calculated as

$$\Delta_f G^\circ_{ox} = \Delta_f H^\circ_{ox} - 298.15\cdot\Delta_f S^\circ_{ox}, \quad (11)$$

using estimated enthalpies and entropies, is also given in Table 1. The combined expanded uncertainty of $\Delta_f G^\circ_{ox}$, is determined by the uncertainty of $\Delta_f H^\circ_{ox}$, which is much higher than that of the entropic term, and is equal to 14 kJ·mol^{-1}. As seen, all the solid solutions studied are stable against their constituting binary oxides. However, the relative stability of $BaZr_{1-x}Pr_xO_3$ decreases with the amount of Pr.

Conclusions

The dependence of the standard enthalpy of formation from binary oxides on the Goldschmidt tolerance factor, $\Delta_f H^\circ_{ox}(t)$, was shown to be linear for a number of perovskite-type $A^{II}B^{IV}O_3$ (A = Ca, Sr, Ba; B = Ti, Zr, Hf, Ce, Pr, Tb, U, Pu, Am) oxides. This dependence was used to predict the $\Delta_f H^\circ_{ox}$ values for praseodymium-substituted barium zirconates $BaZr_{1-x}Pr_xO_3$. The increase in x results in the distortions of the crystal lattice, decreasing the tolerance factor and making $\Delta_f H^\circ_{ox}$ more positive. The values of the enthalpies of mixing, calculated regarding $BaZr_{1-x}Pr_xO_3$ as a solid solution of $BaPrO_3$ in $BaZrO_3$, were found to be indicative of the regular or ideal solution behavior. Thus, to estimate the absolute entropy of $BaZr_{1-x}Pr_xO_3$ using the expression for the entropy of ideal mixing, the absolute entropy of $BaPrO_3$, not yet reported in the literature, had to be estimated first. We found that for some of the $A^{II}B^{IV}O_3$ (A = Ca, Sr, Ba; B = Ti, Zr, Hf, Ce) perovskites, for which the entropy values are known, an almost perfectly linear relationship exists between the relative changes of entropy and molar volume in the reaction of formation of $A^{II}B^{IV}O_3$ from AO and BO_2. This relationship allowed predicting the entropy of $BaPrO_3$ with relative uncertainty of less than 2% of its value, the uncertainty being virtually determined

by the uncertainties of the reference S^{o}_{298} data for the corresponding binary oxides. With the knowledge of $S^{o}_{298}(BaPrO_3)$, not only the absolute entropy values, but also the standard entropies and Gibbs energies of formation of $BaZr_{1-x}Pr_xO_3$ from binary oxides were calculated. The latter, though increasing with x in $BaZr_{1-x}Pr_xO_3$, are negative for all x from 0.0 to 1.0, so $BaZr_{1-x}Pr_xO_3$ should be stable with respect to BaO, ZrO_2 and PrO_2.

The methodology employed in predicting the enthalpy, $\Delta_f H^{\circ}_{ox}$, and, especially, the absolute entropy of $BaZr_{1-x}Pr_xO_3$ can be applied to other similar oxides. We believe that, especially in the absence of experimental data, our work would be of interest to the researchers who are studying the thermodynamics and stability issues of substituted barium zirconates, and that it could provide the data for the future thermodynamic assessments and phase diagram calculations in BaO–ZrO_2–PrO_2 and related oxide systems.

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